Probing the Phase Diagram of $Bi_2Sr_2CaCu_2O_{8+\delta}$ with Tunneling Spectroscopy

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***Abstract*— Tunneling measurements are performed on Ca-rich single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212), with various oxygen doping levels, using a novel point contact method. At 4.2 K, SIN and SIS tunnel junctions are obtained with well-defined quasiparticle peaks, robust dip and hump features and in some cases Josephson currents. The doping dependence of tunneling conductances of Ca-rich Bi2212 are analyzed and compared to stoichiometric Bi2212. A similar profile of energy gap vs. doping concentration is found although the Ca-rich samples have a slighly smaller optimum T_c and therefore smaller gap values for any doping level. The evolution of tunneling conductance peak height to background ratios with hole concentration are compared. For a given doping level, the Ca-rich spectra showed more broadened features compared to the stoichiometric counterparts, most likely due to increased disorder from the excess Ca. Comparison of the dip and hump features has provided some potential insights into their origins.**

I. Introduction

THE peculiar doping dependencies of the superconducting properties of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) has stimulated interest in similar measurements on other high temperature superconductors (HTSs). It is necessary to establish what properties are universal, not only for all high-T_c cuprates, but also for various non-stoichiometric compositions of a particular HTS. It is also useful to consider different doping routes other than oxygen content. The doping dependence of the superconducting energy gap, Δ, is now well established for Bi2212 from tunneling [1], [2] and ARPES [3] studies. The magnitude of the energy gap scales with T_c in the overdoped regime of Bi2212 indicating conventional behavior, however, in the underdoped phase, the energy gap magnitude increases with decreasing hole concentration even as T_c drops to 70 K from its optimal value of 95 K. Furthermore, the robust spectral features, such as dip and hump, also persist over a wide oxygen doping range of Bi2212, which offers a link between these features and the superconductivity mechanism.[4] The tunneling results on Bi2212 also support a novel contention that the doping dependence of the energy gap and the pseudogap temperature T^* closely follow each other suggesting that the pseudogap state is due to precursor superconductivity.[5]

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In the present paper, we investigated the tunneling conductances in $Bi_{2.1}Sr_{1.4}Ca_{1.5}Cu_2O_{8+\delta}$ (Ca-rich Bi2212) by means of superconductor-insulator-normal metal (SIN) and superconductor-insulator-superconductor (SIS) junctions, and compared the results with stoichiometric Bi2212, to obtain information on the influence of the Sr/Ca ratio on the quasiparticle density of states (DOS). It has been previously found that the distances between CuO_2 layers and between SrO and Bi_2O_2 layers along c-axis become shorter as Bi2212 becomes Ca rich. However, the change of the oxygen concentration does not vary any structural parameters.[6] We would expect that the shortening c-axis length increases the coupling between CuO_2 planes, giving a tendency for T_c and the interplane Josephson current to increase, as in the case of uniaxial compression.[7] On the other hand, the excess Ca in the system resides on Sr sites and creates disorder on the SrO planes next to the CuO_2 planes resulting in the decrease of maximum T_c.[8] The two combined effects lead to a system which is sufficiently different from stoichiometric Bi2212 to allow a comparative study.

Magnetic susceptibility studies on Ca-rich Bi2212 indicated that T_{max}, a broad peak in the T-dependent curve of magnetic susceptibility occurring above T_c and T^*, does not depend on the Sr/Ca ratio.[8] The value k_BT_{max} is considered as a characteristic energy for the effective antiferromagnetic (AF) interaction of Cu-spins and the decrease of magnetic susceptibility arises from the gradual development of AF spin fluctuations. It is found that $2\Delta \sim 2k_BT_{max}$ for stoichiometric Bi2212 over a wide doping range. It might be expected therefore that the magnitude of the energy gap in Ca-rich Bi2212 would not change much for a given doping level.[9] The present study sheds light on these issues.

II. Experiment

We grew high quality single crystals of Ca-rich Bi2212 using the floating zone process. As grown crystals have a T_c of 72-74 K with superconducting transition width, ΔT, less than 2 K as measured by ac magnetization. We add extra Bi to the system because of the necessity of excess Bi content for obtaining single phase Bi2212.[10] A maximum T_c, $T_{c,max}$, of 81 K is obtained by annealing in oxygen indicating that $T_{c,max}$ of stoichiometric Bi2212 drops 14 K with excess Ca in the crystal.

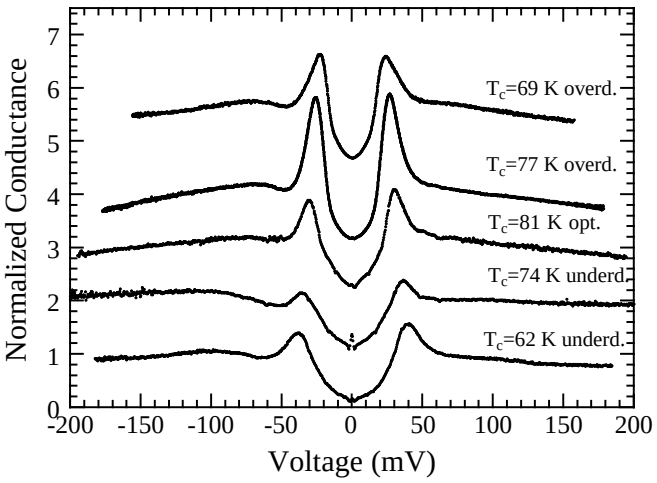

Fig. 1. Tunneling conductances of five SIN junctions on five different Ca-rich Bi2212 crystals, each with a different oxygen concentration. Each spectra is normalized by a constant which is obtained from the high bias conductance value. The data are taken at 4.2 K and shifted for clarity.

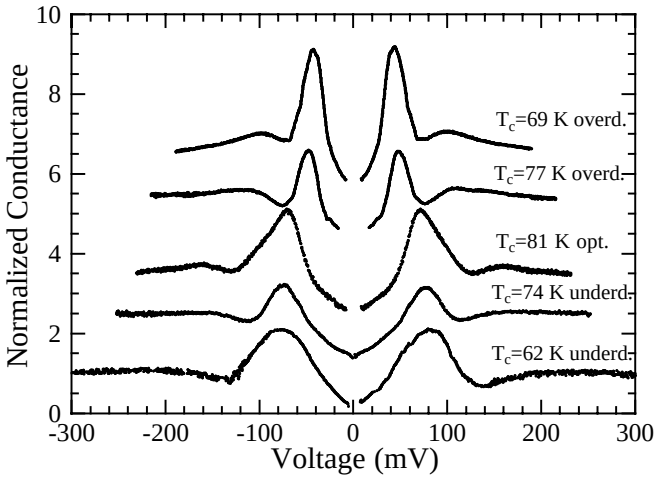

Fig. 2. Tunneling conductances of five representative SIS junctions on five different Ca-rich Bi2212 crystals, each with a different oxygen concentration. The data are taken at 4.2 K. The spectra (except T_c=62 K underdoped) are shifted and Josephson current peaks are removed from the data for clarity.

For this study, the doping range of as grown crystals extended from overdoped (T_c=69 K, ΔT<0.5 K and T_c=77 K, ΔT<0.3 K), optimally doped (T_c=81 K, ΔT<1 K) to the underdoped region (T_c=74 and 72 K ΔT<2 K and T_c=62 K ΔT<1.2 K), where overdoped samples where obtained by annealing in oxygen and underdoped samples by annealing in Ar gas flow. Both SIS break junctions and SIN junctions were prepared on freshly cleaved surfaces by a point contact technique with a Au tip at 4.2 K to reduce any surface contaminations. First SIN junctions are obtained, followed by SIS junctions formed by breaking off a piece of the Bi2212 sample which attaches to the Au tip.[11] $I-V$ and $dI/dV-V$ characteristics are recorded using the conventional lock-in technique.[12]

III. Results and Discussion

Fig. 1 shows the tunneling conductances of five SIN junctions at 4.2 K obtained from five different crystals with T_c=69 and 77 K overdoped, T_c=81 K optimally doped, T_c=74 K and T_c=62 K underdoped. Here and hereafter in figures the voltage is the sample voltage which corresponds to removal of electrons from the superconductor, in other words the negative bias is the occupied quasiparticle states in the DOS. Each spectrum is normalized by a constant and shifted vertically for clarity. Each spectrum exhibits quasiparticle peaks at $eV\sim\pm\Delta$, which indicates different energy gap magnitudes for different hole concentrations. Here it is very important to notice that peculiar spectral features (dip and hump), which are always observed in careful tunneling and ARPES studies, [1], [2], [3], [4], [5], [11], [13], [14], [15] exist over the entire doping range indicating close relation to superconductivity. As the oxygen doping decreases from the overdoped region to the underdoped region, the energy gap magnitude increases as in nonsubstituted crystals of Bi2212. Furthermore, the overall spectral features persist and move out to higher voltages as the gap increases. Except for the particular overdoped T_c=77 K sample, there is a general decrease of the conductance peak height to background ratio with decreasing oxygen concentration, which is consistent with recent ARPES studies which show that the quasiparticle spectral weight is more broadened in the underdoped regime.[3], [16]

A reproducibly obtained characteristic in tunneling studies of stoichiometric Bi2212 is a conductance peak height asymmetry that depends on the hole concentration.[1], [14], [17] In the overdoped regime the peak in the occupied states is considerably higher than the one in the unoccupied states and this cannot be removed from the background by normalization. In the underdoped regime, the asymmetry is just the opposite and the crossover occurs near optimal doping. Recent models of asymmetry in tunneling studies of Bi2212 [18], [19] have suggested that this might be an intrinsic effect. However, another tunneling study of Bi2212 by scanning tunneling microscopy/spectroscopy (STM/STS) shows a more consistent asymmetry between overdoped and underdoped Bi2212.[15] Since the tunneling conductances obtained by STM/STS may be susceptible to an energy dependent background, such effects need to be considered as well. On the other hand, the quasiparticle spectral peaks in Ca-rich Bi2212 in Fig. 1 show an asymmetry whereby the peaks at the unoccupied side of DOS are higher. Only the most overdoped sample exhibits the more standard asymmetry. If there is a shift of the asymmetry, it is occurring somewhere in the overdoped region. Furthermore, for a given doping level (e.g. optimal T_c) the Ca-rich spectra appear more broadened than the stoichiometric spectra. This may be a consequence of the increased disorder from the excess Ca.

It is useful to obtain SIS junctions not only as a consistency check but because the reduced smearing effects in SIS junctions allow a direct measure of the energy gap from the quasiparti-

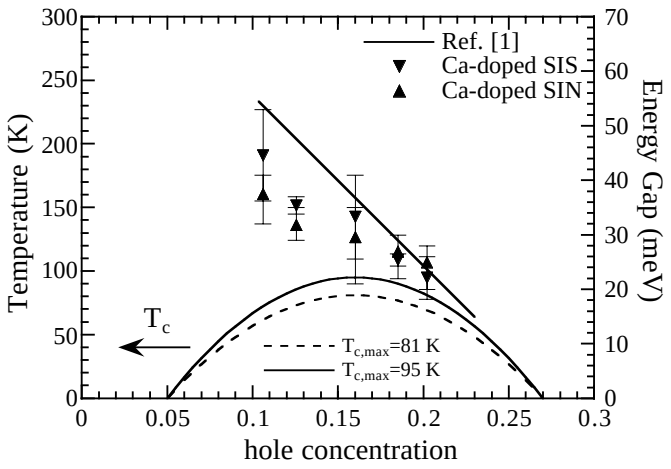

Fig. 3. The phase diagram of the Bi2212 system. The solid and dashed curves correspond to T_c of the stoichiometric and Ca-rich Bi2212 respectively using the emprical formula $T_c/T_{c,max}$=1-82.6(p-0.16)^2. The solid line is the line fit to Ref. [1]. The triangles are the present data which are averages of energy gap values obtained from SIN and SIS tunneling experiments (see legend).

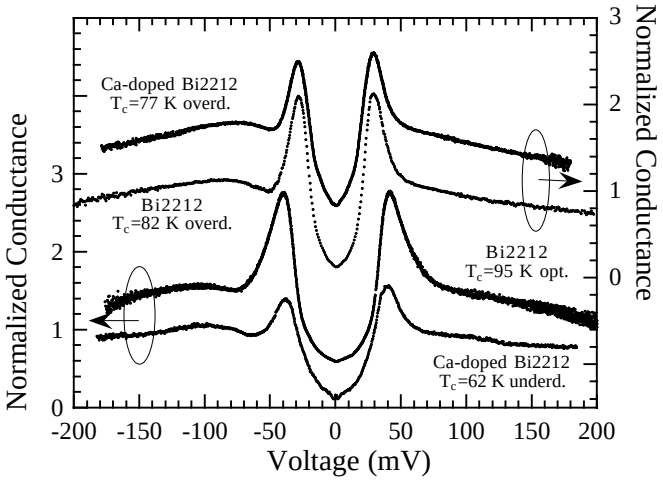

Fig. 4. Comparison of stoichiometric and Ca-rich Bi2212 SIN data. The upper two spectra are overdoped crystals with similar gap values and T_c's. While the lower two spectras have similar gaps, they have different T_c's.

cle peak positions ($\pm 2\Delta$). Also, the high-bias spectral features are amplified in the SIS geometry. Fig. 2 shows normalized tunneling conductance-voltage characteristics of five SIS junctions from five different hole concentrations (T_c=69 and 77 K overdoped, T_c=81 K optimally doped, T_c=74 and 62 K underdoped). These were measured at 4.2 K, normalized by a constant (at 200 mV) and shifted for clarity. The Josephson current peaks are erased for clarity and will not be discussed in this paper. Similar to Fig. 1 which shows SIN junctions, Fig. 2 also reveals an increasing energy gap magnitude with decreasing hole concentration for SIS junctions. At the same time, more pronounced dip and hump structures also shift towards higher energies with underdoping. Note that the peaks correspond to $\pm 2\Delta$ and therefore the characteristic energies of the dip and hump are shifted by an additional Δ. It has been clearly shown that the SIN data can reproduce the SIS spectrum by convoluting it by itself.[1] Some of the SIS spectra exhibit rather large peak widths which may be an indication of an inhomogeneous gap distribution within the junction area.

In Fig. 3 are shown the measured gap values vs. hole concentration in Ca-rich Bi2212. The solid and dashed curve are the T_c for stoichiometric Bi2212 and Ca-rich Bi2212 respectively, where the maximum critical temperature, $T_{c,max}$, is 95 K for stoichiometric Bi2212 and 81 K for Ca-rich Bi2212. The hole concentrations, p, are estimated from the empirical formula $T_c/T_{c,max}$=1-82.6(p-0.16)^2. The solid line is the linear fit to our previously published data.[1] The gap magnitudes are estimated directly from the quasiparticle peaks without any fit to d-wave BCS theory. Contrary to our previous observations on stoichiometric Bi2212 which show similar gap magnitudes for SIN and SIS junctions, in Ca-rich Bi2212 we observed not only a large scattering of energy gap magnitudes, but also an accumulation of averaged gaps at different energy locations for two different types of junction geometry, SIN and SIS. Each hole concentration depicts at least 10 SIN and SIS junctions to get reasonable statistical distribution of the energy gap magnitudes. The gap magnitude average of SIS junctions is larger than the gap magnitude average of SIN junctions in the underdoped range. However, over the wide doping range which is examined, the error bars of both junction geometries lie top of each other. Our use of the peak voltage in SIN junctions leads to an overestimate of the gap, which makes the discrepancy between SIS and SIN gap values a bit larger. The origin of this discrepancy is not known but perhaps the increased defect density in the Ca-rich Bi2212 allows a higher diffusion rate for oxygen. Since the equilibrium oxygen concentration in air leads to slight overdoping, this tendency would give a smaller gap on the surface compared to the bulk, the latter being probed by SIS break junctions.

While the average gap magnitude is smaller than for stoichiometric Bi2212, at least part of this is due to the generally lower T_c value for any hole concentration in Ca-rich Bi2212. Note however that the overall doping dependence shows the same trend, that is, the gap increases in the underdoped region even as T_c decreases.

In order to understand the spectral features of stoichiometric and Ca-rich Bi2212, we compare spectra that have the same gap magnitude. For example, we plotted two overdoped SIN junctions which have similar gap magnitudes in the top part of Fig. 4. Note that the T_c values are not that different. Both tunneling conductances are normalized by a constant and Ca-doped Bi2212 is shifted by 0.7 units. This figure shows that the tunneling conductances are nearly identical, showing the same d-wave like subgap conductance, sharp quasiparticle peaks, and dip/hump features at similar energies. The bottom part of Fig. 4 shows optimally doped T_c=95 K stoichiometric Bi2212 com-

pared with underdoped T_c=62 K Ca-rich Bi2212, both of which have gap values near 40 meV. While the hump energies are nearly the same, the location of the dip feature is considerably different in the two spectra as are the critical temperatures. The latter effect is consistent with previous observations that the dip location follows the neutron resonance mode energy which scales with T_c and not the gap energy.[4] The smaller T_c value of the Ca-rich sample would thereby imply a smaller resonance mode energy which would put the dip location closer to the gap edge. At present these results are qualitative and await further quantitative analysis.

In summary, we have prepared Ca-rich Bi2212 crystals and varied the doping via the oxygen concentration. The optimum T_c value of the Ca-rich samples is 81 K, significantly smaller than the optimum value of 95 K in stoichiometric Bi2212. The key result is that the trend of the energy gap vs. doping is the same in both types of Bi2212. This suggests that this trend is a universal feature of high T_c cuprates. Preliminary analysis of the tunneling spectra suggests that the hump feature scales directly with the energy gap but that the dip feature is tied more closely to the bulk T_c. Such a behavior is consistent with previous investigations which suggest the dip feature is linked to the resonance mode found in neutron scattering.

IV. Acknowledgments

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